



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: **POLYMER NANOCOMPOSITE FORMATION BY EMULSION SYNTHESIS**

(57) Abstract

The formation of a nanocomposite by emulsion polymerization is described. The invention includes the nanocomposite latex, a solid nanocomposite of a layered silicate mineral intercalated with an emulsion polymer and blends of the solid nanocomposite with other polymers.

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POLYMER NANOCOMPOSITE FORMATION BY EMULSION SYNTHESISField of the Invention

This invention relates to composite materials having reduced permeability to small molecules, such as air, and which has enhanced mechanical properties. More particularly this invention relates to layered silicates intercalated with an emulsion polymer.

Background of the Invention

Layered clay minerals such as montmorillonite are composed of silicate layers with a thickness of about 1 nanometer. Dispersions of such layered materials in polymers are frequently referred to as nanocomposites.

Recently, there has been considerable interest in forming nanocomposites as a means to improve the mechanical properties of polymers. Incorporating clay minerals in a polymer matrix, however, does not always result in markedly improved mechanical properties of the polymer. This may be due to the lack of affinity between the layered silicate materials and the organic polymers. Thus it has been proposed to use ionic interactions as a means of incorporating clay minerals in a polymer. In this regard, see, for example U.S. Patent 4,889,885 and U.S. Patent 4,810,734. This type of approach, unfortunately, has limited usefulness. Indeed, a more direct, simple, and economic approach to preparing nanocomposites is highly desirable.

One object of the present invention is to provide a latex comprising a layered silicate intercalated with an emulsion polymer.

Another object of the present invention is to provide a composite material formed from a dispersion latex of a layered silicate and an emulsion polymer which material has reduced permeability to small molecules such as air, and improved mechanical properties.

These and other objects, features and advantages of the present invention will become more apparent from the description which follows.

#### Summary of the Invention

In one embodiment of the present invention, a latex is provided comprising water and a layered mineral intercalated with a polymer emulsion.

Another embodiment of the present invention provides a nanocomposite comprising a layered mineral intercalated with an emulsion polymer.

Another aspect of the present invention comprises a blend of a first polymer with a nanocomposite composed of a layered mineral intercalated with an emulsion polymer.

The process for producing the latex of the present invention comprises forming a dispersion of a layered mineral in water including a swelling agent such as an onium salt, adding a polymerizable monomer or monomers, such as an olefin or diene, with a polymerization initiator to the dispersion, and thereafter polymerizing the monomer or monomers to form a latex comprising water and a polymer nanocomposite. The preparation of this latex comprises yet another embodiment of the present invention.

A composite material formed from the latex of the present invention has improved mechanical properties and reduced air permeability to small molecules such as air making it particularly useful in a range of applications, particularly as a tire liner and as inner tubes, barriers, films, coatings and the like.

#### Detailed Description

Any natural or synthetic layered mineral capable of being intercalated may be employed in the present invention; however,

layered silicate minerals are preferred. The layered silicate minerals that may be employed in the present invention include natural and artificial minerals capable of forming intercalation compounds. Nonlimiting examples of such minerals include smectite clay, montmorillonite, saponite, beidellite, montronite, hectorite, stevensite, vermiculite, and hallosite. Of these montmorillonite is preferred.

The swelling agent used in the practice of the present invention is any compound capable of intercalating the layered mineral and thereby increasing the distance between the layers. Particularly preferred swelling agents are hydrocarbyl onium salts represented by the formulae  $A^-M+R^1R^2R^3R^4$  and  $A^-Py+R^4$  where  $A^-$  denotes an anion such as halide,  $OH^-$ ,  $NO_3^-$ ,  $SO_4^-$  and the like;  $M$  denotes N, S, P;  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently denote hydrogen alkyl, aryl or allyl groups, which may be the same or different, provided at least one of which is other than hydrogen; and  $Py$  denotes the pyridinium or alkyl substituted pyridinium group.

It will be readily appreciated that some of the above mentioned swelling agents are also emulsifying agents. However, in those instances when the swelling agent is not an emulsifying agent preferably an emulsifying agent will be employed in carrying out the polymerization. Optionally, of course, another emulsifying agent may be used even when the swelling agent has emulsifying properties. In either event, the emulsifying agent will be one typically used in emulsion polymerization processes. Cationic emulsifying agents and non-ionic emulsifying agents are preferred.

The polymers and copolymers referred to herein as emulsion polymers are those formed by emulsion polymerization techniques. Included are polymers based on one or more water immiscible, free radical polymerizable, monomers such as olefinic monomers and especially styrene or paramethyl styrene, butadiene, isoprene, chloroprene, and acrylonitrile. Particularly preferred are styrene rubber copolymers, i.e., copolymers of styrene and butadiene, isoprene chloroprene and acrylonitrile. Especially preferred, in the practice of the present invention are homopolymers and copolymers having a glass transition temperature less than about  $25^\circ C$ , a number average

molecular weight above 5,000g/mole and especially above 15,000g/mole. Also, the preferred polymer will contain some unsaturation or other reactive sites for vulcanization.

The latex of an intercalatable mineral having an emulsion polymer intercalated in the mineral is prepared by forming a dispersion of the layered mineral in water and including the swelling agent. Typically, the mineral is first dispersed in water by adding from about 0.01 to about 80 grams of mineral to 100 grams of water and preferably, about 0.1 to about 10.0 g of mineral to 100 g of water, and then vigorously mixing or shearing the mineral and water for a time sufficient to disperse the mineral in the water. Then the hydrocarbyl onium salt is added to the dispersion, preferably as a water solution, and with stirring.

The amount of the onium salt used in the process of the present invention depends on the type of layered material and monomers used as well as process conditions. In general, however, the amount of onium salt used will be in the range of the cation co-exchange capacity of the layered mineral to about 10% to about 2,000% of the cationic exchange capacity of the layered mineral.

Next, the polymer latex is formed by adding to the mineral dispersion an emulsifying agent, if desired or necessary, the appropriate monomer or monomers, and free a radical initiator under emulsion polymerization conditions. For example, styrene and isoprene are polymerized in the mineral dispersion using a free radical polymerization initiator while stirring the reactants. The copolymerization typically is conducted at a temperature in the range of about 25°C to about 100°C and for a time sufficient to form the polymer latex, followed by termination of the reaction.

The latex described above can be used to form coatings or films following standard techniques employed for forming such materials. Additionally, the nanocomposite of the layered silicate mineral and the polymer may be recovered by coagulating the latex, and drying the solid composite. The solid composite can then be formed into tire

inner-liners or inner tubes using conventional processing techniques such as calendering or extrusion followed by building the tire and molding.

In one embodiment of the present invention the nanocomposite is dispersed with another polymer, such as a styrene-rubber copolymer by blending on a rubber mill or in an internal mixer. Preferably the nanocomposite will be blended with a polymer formed from the same monomer or monomers used in forming the nanocomposite. The amount of the nanocomposite in the polymer typically will be in the range of about 0.1 to about 70 wt.%.

In producing tire inner liners the polymer blended with the nanocomposite of this invention preferably will have a molecular weight of greater than about 10,000 and some unsaturation or other reactive sites so that it can be vulcanized or cross-linked in the bulk state.

The invention will be more clearly understood by reference to the following examples.

#### Example 1

A layered silicate, montmorillonite clay (18g), was slurried with water (450g) which had been degassed by sparging with nitrogen. The slurry was stirred overnight at 23°C. The clay was dispersed in the water in a Waring blender for three minutes and then degassed further. Dodecyl trimethyl ammonium bromide (25.7g) was dissolved in degassed water (250g) and added to the clay slurry. Isoprene (35g), styrene (15g), and azobisisobutyronitrile (AIBN) (0.25g) as initiator were blended and then added to the clay slurry. The mixture was mechanically stirred for 20 hours at 23°C and for 26 hours at 65°C at which time polymerization was terminated with a 5g aliquot of a mixture of (0.24g) 2,6-di-tert-butyl-4-methylphenol, (1.6g) hydroquinone, (0.8g) tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane and 200 ml methanol. The net result was the

formation of an emulsion containing a layered silicate having a styrene-isoprene copolymer latex intercalated in the layered mineral.

Example 2

A solid nanocomposite was formed from the latex of Example 1 by adding an excess of methanol to the latex, separating the solid from the liquid aqueous phase and washing the solid six times with methanol, followed by drying for about 18 hours at 60°C under vacuum and for 48 hours at 23°C in vacuum.

Example 3

A portion of the solid nanocomposite (20 grams) of Example 2 was then melt blended at 130°C in a Brabender mixer for 5 minutes with a styrene-isoprene copolymer (20 grams) that was synthesized identically but had no clay. The blend of nanocomposite and the clay-free styrene-isoprene copolymer was cross-linked by roll milling the blend with stearic acid (1 phr), zinc oxide (3.9 phr), and tetramethyl thiuram disulfide (accelerator) (1 phr) at 55°C for ten minutes. Then the blend was hot pressed into 20 mil films and cured for 20 minutes at 130°C. The films were tested on a Mocon 2/20 for oxygen transmission at 30°C. The results are given in Table I below. Also shown in Table I were the results obtained with a film formed from a styrene-isoprene copolymer that had been synthesized identically but had no clay. (Comparative Example 1)

Uniaxial tensile properties were also measured on mini-tensile film specimens using an Instron tester. The stress-strain measurements were performed at room temperature and at an extension rate of 0.51 mm/min and the results are shown in Table 2 below. Also shown in Table 2 and labeled as Comparative Example 1 are the tensile properties obtained for a polystyrene-isoprene copolymer that was synthesized identically to that in Example 1 but had no clay.

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TABLE 1

<u>Film</u>	<u>Wt% Clay</u>	<u>Oxygen Transmission</u>	$\frac{\text{cm}^3 \times \text{MILS}^*}{\text{m}^2 \times 24 \text{ hr.}}$
Example 3	26.3	4,138	
Comparative		12,340	
Example 1	0		

\*Mocon 2/20 @ 30°C

TABLE 2

Stress at Break (psi)	Strain at Break (%)	Youngs Modulus (psi)	Modulus (psi)	100%	Modulus (psi)	Modulus (psi)	300%	Modulus (psi)	400%	Modulus (psi)	Energy at Break (in-lbs.)
				200%			Modulus (psi)		Modulus (psi)		
<u>Film</u>											
Comparative 1	2001	560	2053	503	660	901	1236	12.1			
Example 3	2312	497	5018	699	880	1262	1727	11.3			

## CLAIMS:

1. A latex comprising: water and a layered mineral intercalated with a an emulsion polymer.
2. The latex of claim 1 wherein the layered mineral is a natural or synthetic mineral selected from the group consisting of smectite clay, montmorillonite, saponite, beidellite, montronite, hectorite, stevensite, vermiculite, and hallosite.
3. The latex of claim 1 wherein the polymer is formed from a free radical polymerizable olefinic monomer or monomers
4. The latex of claim 1 wherein the polymer is a styrene-containing copolymer.
5. The latex of claim 4, wherein the copolymer contains a comonomer selected from the group consisting of butadiene, isoprene, chloroprene and acrylonitrile.
6. The latex of claim 5 wherein the layered material is montmorillonite.
7. A latex comprising:  
water and a natural or synthetic layered mineral intercalated with a polymer or copolymer, wherein the layered mineral is selected from the group consisting of smectite clay, montmorillonite, saponite, beidellite, montronite, hectorite, stevensite, vermiculite, and hallosite and wherein the polymer or copolymer is formed from a free radical polymerizable olefinic monomer or monomers.
8. The latex of claim 7, wherein the olefinic monomer or monomers are selected from the group consisting of styrene, para-methylstyrene, butadiene, isoprene, chloroprene and acrylonitrile.

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9. A nanocomposite comprising a layered mineral intercalated with an emulsion polymer.

10. The nanocomposite of claim 9 wherein the layered mineral is selected from the group consisting of smectite clay, montmorillonite, saponite, beidellite, montronite, hectorite, stevensite, vermiculite, and hallosite.

11. The nanocomposite of claim 10, wherein the polymer is formed from a free radical polymerizable olefinic monomer or monomers.

12. The nanocomposite of claim 11, wherein the polymer is a styrene-containing copolymer.

13. The nanocomposite of claim 12, wherein the styrene-containing copolymer is a copolymer of styrene or paramethyl styrene with a monomer selected from the group consisting of butadiene, isoprene, chloroprene, and acrylonitrile.

14. The nanocomposite of claim 13 wherein the layered mineral is montmorillonite.

15. A polymer blend which comprises:

a first polymer and a nanocomposite of a layered mineral intercalated with an emulsion polymer.

16. The blend of claim 15 wherein the first and emulsion polymers are formed from the same monomer or monomers.

17. The blend of claim 16 wherein the first and emulsion polymers are copolymers.

18. The blend of claim 17 wherein the amount of nanocomposite in the blend is in the range from about 0.1 to about 70 wt.%.

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19. The blend of claim 18 wherein the copolymer is a copolymer of styrene or paramethyl styrene with a monomer selected from butadiene, isoprene, chloroprene and acrylonitrile.

20. A process for producing a latex including a nanocomposite material which comprises:

dispersing a layered mineral in water to form a dispersion;

adding a swelling agent to the dispersion; and thereafter

polymerizing a free radical polymerizable olefinic monomer or monomers in the presence of the dispersion under emulsion polymerization conditions to form a latex including the nanocomposite material.

21. The process of claim 20 wherein two monomers are copolymerized, one being a styrene or paramethylstyrene monomer and the other being butadiene, isoprene, chloroprene, or acrylonitrile.

22. The process of claim 21 wherein the swelling agent is a hydrocarbyl onium salt.

23. The process of claim 22 wherein the hydrocarbyl onium salt has the formula  $A-M^+R^1R^2R^3R^4$ , or  $A-Py^+R^4$  wherein or  $A^-$  is an anion;  $M$  is N, S, or P;  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  independently denotes the same or different hydrogen, alkyl, aryl or allyl groups, and  $Py$  denotes a pridinium or an alkyl substituted pyridium group.

24. The process of claim 23 wherein the polymerization is conducted in the presence of an emulsifying agent at a temperature in the range of about 5°C to about 100°C for a time sufficient to form the latex.

25. The process of claim 24 including adding a coagulating agent to the latex to coagulate solid nanocomposite and thereafter separating the solid nanocomposite.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/07226

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08L 7/02; C08K 3/34.

US CL :524/ 445, 446, 447, 449, 534, 789, 791, 856.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/ 445, 446, 447, 449, 534, 789, 791, 856.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,889,885 A (USUKI ET AL) 26 December 1989, column 2, lines 34-60; column 4, lines 29-53; column 5, lines 8-34.	1-25
Y	US 4,472,538 A (KAMIGAITO ET AL.) 18 September 1984, column 1, lines 11-24; column 2, lines 36-50.	1-25
Y	US 4,810,734 A (KAWASUMI ET AL.) 07 March 1989, column 1, lines 6-15; column 2, lines 40-68; column 3, lines 18-31; column 4, lines 12-32; column 5, lines 40-54.	1-25

Further documents are listed in the continuation of Box C.  See patent family annex.

Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
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"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 AUGUST 1996	16 SEP 1996

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JOHN J. GUARIELLO Telephone No. (703) 308-2351
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**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US96/07226**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

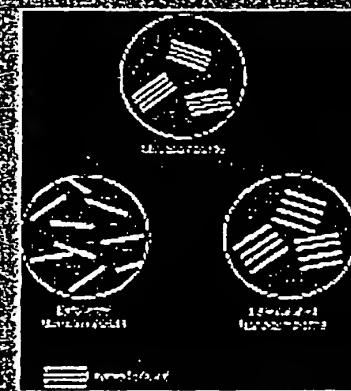
This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-14, 20-25, drawn to a latex composition and the method of making the latex composition.

Group II, claim(s) 15-19, drawn to a polymer blend composition.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the process for producing the polymer blend is not required to produce the aqueous latex composition in Group I. The process of Group I cannot produce the polymer blend of Group II since Group I has a polymer and additive which is not a polymer for a blend. The process for making the first recited product is not required to make the second required product since the second product is a polymer blend whereas the first product is not a polymer blend.

**Review.** Polymers filled with low amounts of layered silicate dispersed at nanoscale level are most promising materials characterized by a combination of chemical, physical, and mechanical properties that cannot be obtained with macro- or microscopic dispersions of organic fillers. Polymer layered silicate nanocomposites can be obtained by insertion of polymer molecules in the galleries between the layers of phyllosilicate. Here, hydroxylated alkaline earth metal cations are chosen which neutralize the negative charge resulting from isomorphous substitutions of Mg and Al cations within the silicate interlayer. Some polymers molecules can prepare intercalation hybrids when the cations (Li<sup>+</sup>) replacing the water molecules in the galleries by polymers containing polar functional groups using the so-called ion-dipole method. A more general technique involves compatibilization of the silicate with intercalation of organic molecules. Typically, an organic molecule (e.g., aliphatic chain of the OLS) favors the intercalation of any type of polymer. Intercalated or delaminated polymer-silicate hybrids are obtained depending on whether the stack organization of the silicate layers is preserved or is lost, with single sheets being distributed in the polymer matrix. The method currently used for preparing polymer-layered silicate (PLS) nanocomposites are: in situ polymerization from polymer solution or from polymer melt. Although PLS nanocomposites have been known for a long time, the possibility of preparing thermoplastic nanocomposites of OLS is processing. In this boosting the present interest in these materials and their properties. Some PLS nanocomposites have been characterized by DSC, thermogravimetry, transmission electron microscopy, differential scanning calorimetry, and NMR. Published results on PLS nanocomposites are reviewed concerning their characteristics, properties, and applications, in particular, in the field of polymer processing.



## Polymer layered silicate nanocomposites

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### Introduction

The expansion of industrial and economic activities results in a continuous demand for new, low-cost materials able to meet increasingly stringent conditions. Polymers are commonly admixed with a variety of both natural and synthetic compounds to improve their performance. Inorganic components used for this purpose are called "fillers" and give rise to "filled polymers"<sup>1)</sup> with greater mechanical strength or impact resistance, or

reduced electrical conductivity or permeability to gases, such as oxygen, and moisture. In these conventional materials, there is a distinct macroscopic separation between the organic and the inorganic phase without any significant interactions between them. Microscopic dispersion is the most that can be achieved by treating the surface of the inorganic material.

Nanocomposites, on the other hand, constitute a new class of materials with an ultrafine phase dispersion (e.g. of clay) of the order of a few nanometers that endows them with unique properties not shared by conventional materials and offers new technological and economic opportunities<sup>2)</sup>.

\* Guest researcher from the Institute of Biochemical Physics of Russian Academy of Sciences, 117978, Kosygin 4, Moscow, Russia.

Nanocomposites preparation, characterization and properties have been previously reviewed by: Mühlhaupt<sup>3,4)</sup>, Giannelis<sup>5)</sup>, Lagaly<sup>6)</sup> and Frisch<sup>7)</sup>.

Nanocomposites can be classified depending on the shape of the nanofiller. Particles are characterized by a three-dimensional nanosize distribution whereas in nanotubes or whiskers nanosize is limited to two dimensions in space. Finally, in the case of phyllosilicates (e.g. clay) single silicate layers with one-dimensional nanosize can be dispersed in the polymer.

One of the earliest systematic studies of the interaction between a clay mineral and a macromolecule dates back to 1949, when Bower described the absorption of DNA by montmorillonite<sup>8)</sup>. Even in the absence of X-ray diffraction (XRD) evidence, this finding implied insertion of the macromolecule in the lamellar structure of the silicate. In the case of synthetic polymers, Uskov<sup>9)</sup> in 1960 found that the softening point of poly(methyl acrylate) derived by polymerization of methyl methacrylate was raised by montmorillonite modified with octadecylammonium, while in the following year Blumstein<sup>10)</sup> obtained a polymer inserted in the structure of a montmorillonite by polymerizing a previously inserted vinyl monomer. Two years later, Greenland<sup>11)</sup> used a poly(vinyl alcohol)/montmorillonite system to show that a polymer could be directly inserted in a clay in an aqueous solution. In 1975, Tanihara & Nakagawa<sup>12)</sup> reached a similar result by intercalating polyacrylamide and poly(ethylene oxide) from an aqueous solution. Most pioneering work in clay-polymer nanodispersed systems involved water soluble polymers<sup>13)</sup>. These studies and their developments, date back to 1960's and 1970's, were reviewed by Theng<sup>13)</sup>.

It was not until 1988, however, that the first industrial application was provided by Okada et al.<sup>14)</sup> at Toyota's central research laboratories in Japan. In this case a Nylon 6 nanocomposite was formed by polymerization in the presence of the inserted monomer. This material was then marketed by UBE Industries and Bayer. It is currently used to make the timing belt cover of Toyota's car engines and for the production of packaging film.

### Structure and properties of phyllosilicate

Polymer layered silicate (PLS) nanocomposites are a hybrid between an organic phase (the polymer) and an inorganic phase (the silicate). The choice of the silicate determines the nanoscopic dispersion typical of nanocomposites. The silicates employed belong to the family of layered silicates also known as phyllosilicates, such as mica, talc, montmorillonite, vermiculite, hectorite, saponite, etc.<sup>15,16)</sup> Their crystalline structure consists of a two-dimensional layer obtained by blending two tetrahedral silica laminae with metal atoms (i.e. Mg for talc and Al for mica) to form a corresponding octahedral metal oxide lamina (Fig. 1). Each layer is separated from its neighbors

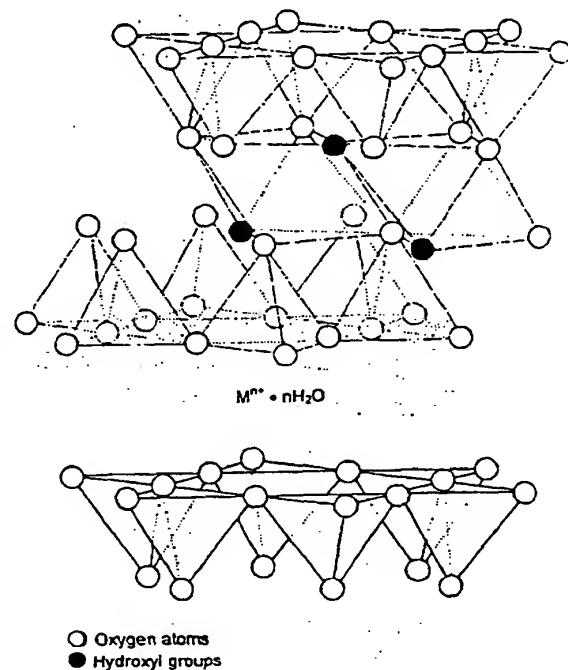


Fig. 1. Idealized structure of 2:1 layered silicate showing two tetrahedral-site sheets (containing silicon and sometimes aluminum) fused to an octahedral-site sheet. (containing aluminum or magnesium)

by a van der Waals gap called a gallery or interstratum. These galleries are usually occupied by cations that counterbalance the negative charge generated by the isomorphous substitution of the atoms forming the crystal ( $Mg^{2+}$  in the place of  $Al^{3+}$  in montmorillonite or  $Li^+$  instead of  $Mg^{2+}$  in hectorite). These cations are normally hydrated alkaline and alkaline-earth metal cations.

In an ordinary Na-O bond, the distance between the atoms is of the order of 2.1–2.2 Å, whereas in a gallery it is 3.6 Å. Since the Coulombic interaction is inversely proportional to the square of the distance between the charges, it is clear that about 60% of the bonding strength between the cation and oxygen is not used. The partial positive charge thus formed for each cation within a gallery makes it highly hydrophilous. Montmorillonite, for example, possesses a considerable hydration energy. The large amount of water it can hold in its galleries neutralizes these partial charges by ion-dipole interactions.

Organic molecules or polymers containing functional groups with partial negative charges, such as carboxyl, hydroxyl, ester, ether, aldehyde and ketone groups, displace the water molecules. The result of this substitution is an organic/inorganic material called an "intercalation hybrid" and the preparation technology that exploits this principle is known as the ion-dipole method<sup>17,18)</sup>. The term "intercalation" is usually associated with periods